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CORRECTION FOR LOSS EFFECTS IN VALENCE-BAND XPS

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TECHNICAL REPORT #5

CORRECTION FOR LOSS EFFECTS IN VALENCE-BAND
XPS SPECTRA BY DECONVOLUTION

by

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ABSTRACT

We present XPS valence band spectra for GaAs(110) and GeSe(001) that have been corrected for coherent loss effects by deconvolution of an instrument/loss function that includes a source function for an unmonochromatized source, a backscattered-electron spectrum to account for energy losses, and an analyzer function. The results are compared with background-subtracted spectra. The deconvolution yields spectra that have significantly greater intensity deep in the band, bringing measurements into closer agreement with theory than is achieved with background subtraction.

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INTRODUCTION

X-ray photoelectron spectroscopy (XPS) is commonly used for probing the electronic and chemical properties of surfaces and shallow interfaces. In addition to the obvious use of core-level spectra for elemental and chemical identification of species in the volume of sample contributing to the photoelectron signal, valence band spectra can be quite useful in understanding the near-surface electronic density of states. Changes in the density of filled states can occur with different surface structural as well as chemical conditions, and, as a result, observations of small changes in the density of states at the surface often can be associated with changes in reactivity, with localized electronic states, or with surface stoichiometry. In many cases, the precision with which such information can be obtained is limited by the resolution in the measurements.

In addition to the obvious broadening that the limited response of any instrument has on a measurement, electron spectroscopies in general are subject to nonsymmetric spectral distortions caused by the transport of electrons out of the solid. These cause a loss in resolution that in part can be regained by accounting for the losses. In this paper, we apply a deconvolution procedure to XPS valence band spectra to remove properly losses and instrumental broadening in such spectra, and as a result, extract what we believe is a true XPS transition density of valence band states in GaAs(110) and GeSe(001).

Broadening mechanisms can be classified as due to the analyzer, the source, or the transport of electrons out of the solid. The first is due simply to the finite band pass of the analyzer. The second is due to the

finite width of the energy levels involved in the production of the x-rays that irradiate the sample. This generally has a simple Lorentzian form. For unmonochromatized sources, there will additionally be satellite x-ray lines that can be considered part of the "broadening" in that they cause extraneous features to appear in a spectrum. Finally, the contribution due to losses suffered by electrons during transport out of the solid gives an asymmetric contribution that can lead to distortions and spurious features at the low-energy side of any line in the spectrum. All of these broadening mechanisms are coherent with the actual signal, i.e., the broadening contributions can not simply be subtracted or divided out, but must, in fact, be deconvoluted from the measured spectrum. Deconvolution of these broadening contributions results in an increase in resolution and a decrease in "background" signal.

The relative importance of these different broadening contributions depends on the features being measured. For two close-lying sharp core levels, the source and analyzer broadening are obviously more important than the energy loss tail; on the other hand, for broad spectra such as valence bands, coherent energy losses can have a significant effect on the shape of the spectral features. Several attempts have been made to remove coherent energy losses from valence band spectra^(1,2). However, even the best of these,⁽²⁾ in which the background is assumed to be proportional to the integrated intensity of features at higher energies, does not allow for structure in the loss spectrum, e.g., due to plasmons, and subtracts only an averaged value for these losses. Deconvolution on the other hand, can remove the structure associated with the loss spectrum. This has been amply demonstrated in applications to Auger line shapes.⁽³⁻⁶⁾ Background subtraction also does nothing to enhance the resolution of the measured spectra, a feature inherent in deconvolution.

In the deconvolution procedure that is used, originally suggested by Mularie and Peria⁽⁷⁾ and developed by Houston and Madden^(3,8), the energy loss broadening and analyzer broadening are modeled by a backscattered-electron spectrum taken at the same experimental conditions as the data and with a kinetic energy for the elastic peak equal to that of the spectroscopic feature of interest. It is assumed that the backscattered-electron spectrum adequately represents the true loss processes occurring in the solid. The latter must, in principle, be different than those in a backscattered-electron spectrum, because both the nature of the excitation and the transport are somewhat different.

In this paper we construct an instrument/loss function and deconvolute it from measured valence band spectra. We include in the instrument function an x-ray source contribution that accounts for source broadening and achromaticity. We show that this is especially beneficial for elements having shallow core levels lying within 10eV of the valence band. We compare results of the deconvolution of valence band spectra for GaAs(110) and GeSe(001) with background subtraction schemes. The next section describes the experimental conditions and Sec. III gives the results of the measurements. The deconvolution and background subtractions are compared in Sec. IV. Sec. V gives a brief summary.

II. EXPERIMENTAL

XPS and UPS measurements, using an unmonochromatized Al source, were made on GaAs(110) and GeSe(001). The GaAs measurements were made on an undoped crystal that was cleaved using a knife edge. Pressures were in the 10^{-10} to 10^{-8} Pa range. The GeSe data were taken in the same UHV system, but with the sample cleaver removed and replaced by a sample preparation induction chamber held at a pressure of 10^{-6} Torr.

The samples were cleaved by pulling on a small wire loop glued to the surface with UHV epoxy, and inserted immediately from this chamber into the UHV chamber. GeSe is easily cleaved and its surface is quite unreactive. No surface contamination was detected with Auger spectroscopy on either sample.

Measurements were made with a PEI double-pass cylindrical mirror analyzer (CMA) with retarding grids, operated at a pass energy of 50 eV, corresponding to an analyzer resolution of ~ 1.5 eV. The data were collected on a Nicolet 1070 signal averager using standard pulse counting techniques for periods of 1/2 to 1 hour. Backscattered-electron spectra were taken with the same experimental parameters used for the valence band spectra, with an elastic peak energy, E_p , near the kinetic energy of the valence band photoelectrons, i.e., $E_p \sim 1485$ eV. The two spectra were then transferred to a computer for analysis. The procedure for deconvoluting XPS measurements is shown schematically in Fig. 1. Briefly, the backscattered-electron spectrum approximates the broadening due to losses experienced by the photoelectrons as they propagate through the lattice and across the surface, as well as the broadening due to the finite energy resolution of the analyzer. Additional broadening of the spectra due to the width of the Al $K\alpha_{12}$ line used to irradiate the surface is included by convoluting the backscattered-electron spectrum with a generated source function corresponding to our Al anode.⁽⁹⁾ This corrects also for the $K\alpha_{34}$ satellite line, which can mask weak features if they occur within ~ 10 eV higher kinetic energy of a much stronger line. Compounds containing Ga are examples where the 3d satellite line can mask features in the valence band spectrum.

The total instrument/loss function thus generated accounts for the three major distortions of the measurement. Because the signal-to-noise ratio of our data is relatively low, both they and the total instrument/loss function are smoothed using a polynomial least square procedure.⁽¹⁰⁾ The instrument/loss function is then deconvoluted from the data with the deconvolution method.⁽¹¹⁾

We also the technologically important compounds of Ga, In, and Al. The binding energy of the highest core level is only 15 to 20 eV. A valence-band measurement taken with an achromatic source will contain a contribution of the $K\alpha_{34}$ satellite line of this core level over at least part of the energy range. Fig. 2 shows the instrument/loss function that corresponds to the valence band of GaAs(110) excited with an Al anode and measured with a CMA at 50 eV pass energy. It is the convolution of an Al anode source function⁽⁹⁾ and a backscattered-electron spectrum at a kinetic energy of 1485 eV measured by the CMA with the same pass energy and at the same geometry. Fig. 3a shows the valence-band measurements for GaAs(110) taken with the monochromatized Al source. This spectrum contains the usual "flat background". In addition, the $K\alpha_{34}$ satellite line of the Ga 3d core level at a binding energy of ~ 8 eV and masks the valence band features in a region several eV wide.

Deconvolution of the spectrum in Fig. 2 from that in Fig. 3a gives Fig. 3c, the final transition density of valence band states for GaAs(110). Fig. 3a consists with a background subtraction scheme, which will be discussed in the next section.

Fig. 4 shows similar results for GeSe(001). In GeSe the shallowest core level is deep enough so that there is no interference of the 3d $K\alpha_{34}$ satellite line with the valence band. Thus only resolution and sensitivity factors govern the choice of source. Fig. 4a is the measured spectrum. The sharp peak at 20 eV binding energy is the $K\alpha_{34}$ satellite line of the Ga source. The usual rising "background" is again observed. Fig. 4d shows the final valence band density of states for GeSe(001) obtained by deconvoluting from the data of Fig. 4a a spectrum similar to that in Fig. 2, but taken on GeSe(001). Figs. 4b and 4c are results of background subtraction and are discussed in the next section.

IV. DISCUSSION

In this section we compare the deconvoluted spectra with spectra resulting when a background subtraction is applied to the data. We first consider the data, shown so far, that are taken with an unmonochromatized source. We then consider spectra taken with a monochromatized source. Finally, we briefly compare the resulting spectra with theoretical expectations for the valence bands of these materials.

Figs. 3 and 4 showed "background"-subtracted spectra for GaAs(110) and GeSe(001) valence band measurements respectively that were taken with an unmonochromatized source. The "background" subtraction is that due to Shirley.⁽²⁾ It assumes that the intensity of the losses at any energy is proportional in some way to the integrated intensity of features at higher energy. The second-order correction⁽²⁾ to the background is shown by the dotted line in Fig. 3a. Fig. 3b is the resulting background-subtracted spectrum. It is obvious that a background subtraction can do nothing to eliminate incoherent features like the Ga 3d $K\alpha_{34}$ satellite line. Fig. 4a shows the same background subtraction as the dotted line, and a first-order

tion⁽¹⁾ as the dashed line. Figs. 4b and 4c are the corresponding background-subtracted spectra for the GeSe(001). Although the Ge 3d $K\alpha_{34}$ satellite line is of course again not removed, it does not interfere with valence-band features. However, it is evident that a background subtraction does nothing to retrieve the proper resolution of the features.

These latter results are reinforced with data taken with monochromatized radiation. Satellite lines are now no longer a problem, and the only questions are those of resolution and relative intensities of features in the spectrum. Fig. 5 shows a GaAs valence band spectrum taken with monochromatized Al radiation,⁽¹²⁾ along with the results for the first- and second-order background subtraction.⁽²⁾ Figs. 5b and 5c can be compared directly with Fig. 3c. The curves are normalized to the leading-peak intensity. It can be seen that the relative intensities of the peaks are quite different (in fact, the second-order background subtraction leads to some negative values), with the background subtraction generally giving smaller intensities for the higher-binding energy features of the spectrum and a lower peak-to-valley distance than is observed with deconvolution. This is a common feature with the deconvoluted spectra: the absolute intensity of higher-binding energy features is higher and the peak-to-valley distance greater than with background subtracted spectra. The difference between deconvoluted and background-subtracted spectra for a given spectral feature becomes more significant the smaller that feature was in the original data. Also the resolution of the deconvoluted results of Fig. 3c is better than that of the subtracted results of Figs. 5b or 5c, even though the latter were taken at initially higher resolution. This is obviously because the background

subtraction does nothing to remove the broadening contribution of the analyzer in these spectra. There is also a ~ 0.5 eV difference in the absolute energy scale, presumably due to a wrong work function in one of the spectra.

The same conclusions are obtained when XPS spectra for GeSe(001) taken with monochromatized Al radiation⁽¹³⁾ that have had a background subtracted are compared with the deconvoluted results of Fig. 4d. There is little difference in resolution as long as a very narrow band width detector is used, but because of the asymmetrically distributed losses, features at higher binding energies have too low an intensity and too low an intensity difference between peaks and valleys.

We briefly compare these results with theoretical expectations. Generally it is found that calculations for the valence band density of states at a surface are higher for the lower-lying peaks than the experiment shows. This difference is usually ascribed to small oscillator strengths for these peaks.⁽¹⁴⁾ The present results show that the differences may lie partly in improper interpretation of the actual intensity of the measured peaks. The relative peak area in the measurement depends both on the relative population of the states making up different peaks and the oscillator strengths. A possible model for the relative peak areas in the density of states, which should be reasonably accurate if there is little hybridization of s and p states, as in GeSe, is obtained by simple bond counting. If one includes relative photoelectron excitation cross sections⁽¹⁵⁾, it can be shown⁽¹⁶⁾ that the agreement is much better with the deconvoluted results than with the subtracted results. Table 1 gives a comparison for GeSe(001). Improved comparisons are also obtained with calculated densities of states.⁽¹⁴⁾

V. SUMMARY

We have applied a deconvolution procedure for eliminating the instrument/loss function from valence-band XPS spectra. We have demonstrated that this has a significant effect on the relative intensities of lower-lying features in the valence band, even in cases where the initial resolution is quite good. Additionally, a deconvolution scheme allows recovery of much of the structure lost by making measurements at lower resolution (for example, to increase sensitivity). It also permits measurements with an unmonochromatized source on materials with shallow core levels, where the uncorrected valence band spectrum shows interference due to the $K\alpha_{34}$ satellite line of the shallow core level.

Peak positions in the deconvoluted spectrum are not significantly different from the background-subtracted spectrum and thus the simpler (although incorrect) method of background subtraction will suffice if only peak positions need to be known. However, if relative intensities are important, only the deconvolution procedure can provide the proper results.

Finally, there is the question of how well the instrument/loss function models the actual processes occurring in the photoelectron excitation, emission, and measurement process. Particularly, the use of a backscattered-electron spectrum for modeling the loss process needs to be examined. We have made comparisons on UPS valence band spectra with an instrument/loss function containing a backscattered-electron spectrum and one containing a core level energy loss spectrum at the proper kinetic energy (using synchrotron radiation), and find little difference for kinetic energies above ~ 100 eV. These results are presented elsewhere.⁽¹⁷⁾ We thus expect that for the present XPS measurements the instrument/loss function containing

a backscattered-electron spectrum is a reasonably accurate representation of the actual losses. It thus becomes a fairly simple matter to generate the instrument/loss function for any instrument and perform the necessary deconvolutions.

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TABLE I

Ratio of Valence Band Peak Areas in GeSe(001).

	C:B:A
DOS (from bond counting)	1:1:3
DOS with cross sectional dependence (Ref. 15)	1.4:1:2.3
deconvoluted results	1.4:1:2.2
subtracted results	
monochromatized Al source (Ref. 13)	2.3:1:10.5

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FIGURE CAPTIONS

1. Schematic diagram of the procedure to obtain XPS valence band line shapes.
2. The instrument/loss function for GaAs(110) valence band spectra excited with unmonochromatized Al $K\alpha$ radiation. The kinetic energy of the main peak in the spectrum is 1485 eV.
3. (a) XPS valence band measurements of GaAs (110) using an achromatic Al source. (b) Subtracted results using the second-order background subtraction of Ref. 2. (c) Deconvoluted results using the instrument/loss function shown in Fig. 2.
4. (a) XPS valence band measurements of GeSe (001) using an achromatic Al source. (b) Spectrum with first-order background subtraction of Ref. 2. (c) Spectrum using the second-order background subtraction. (d) Spectrum after deconvolution using an instrument/loss function similar to Fig. 2, but for GeSe(001).
5. (a) High resolution XPS valence band measurements of GaAs(110) using a monochromatized Al source (Ref. 12). The background approximations are the same as in Fig. 4. (b), (c) Spectrum with first-order and second-order background subtraction, respectively (Ref. 2).

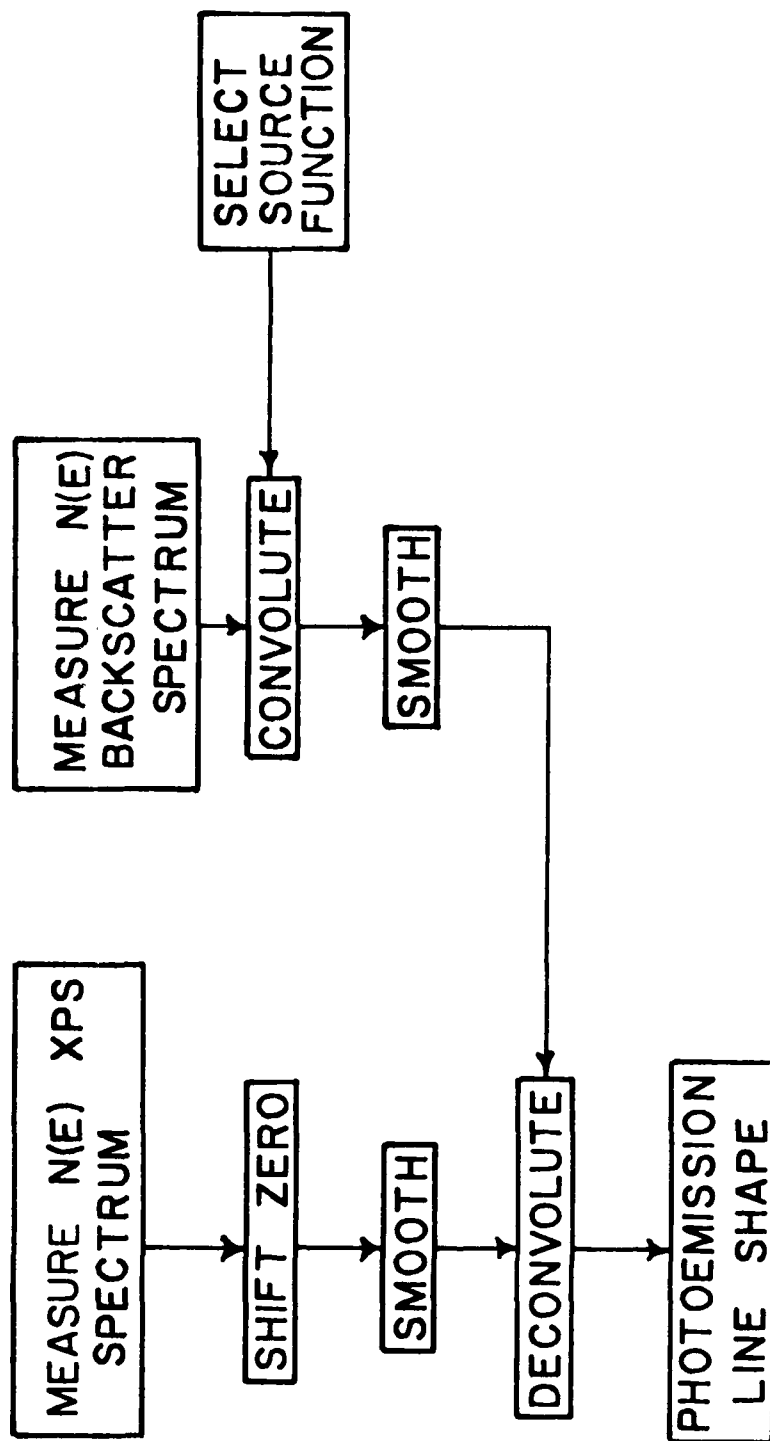


Figure 1.

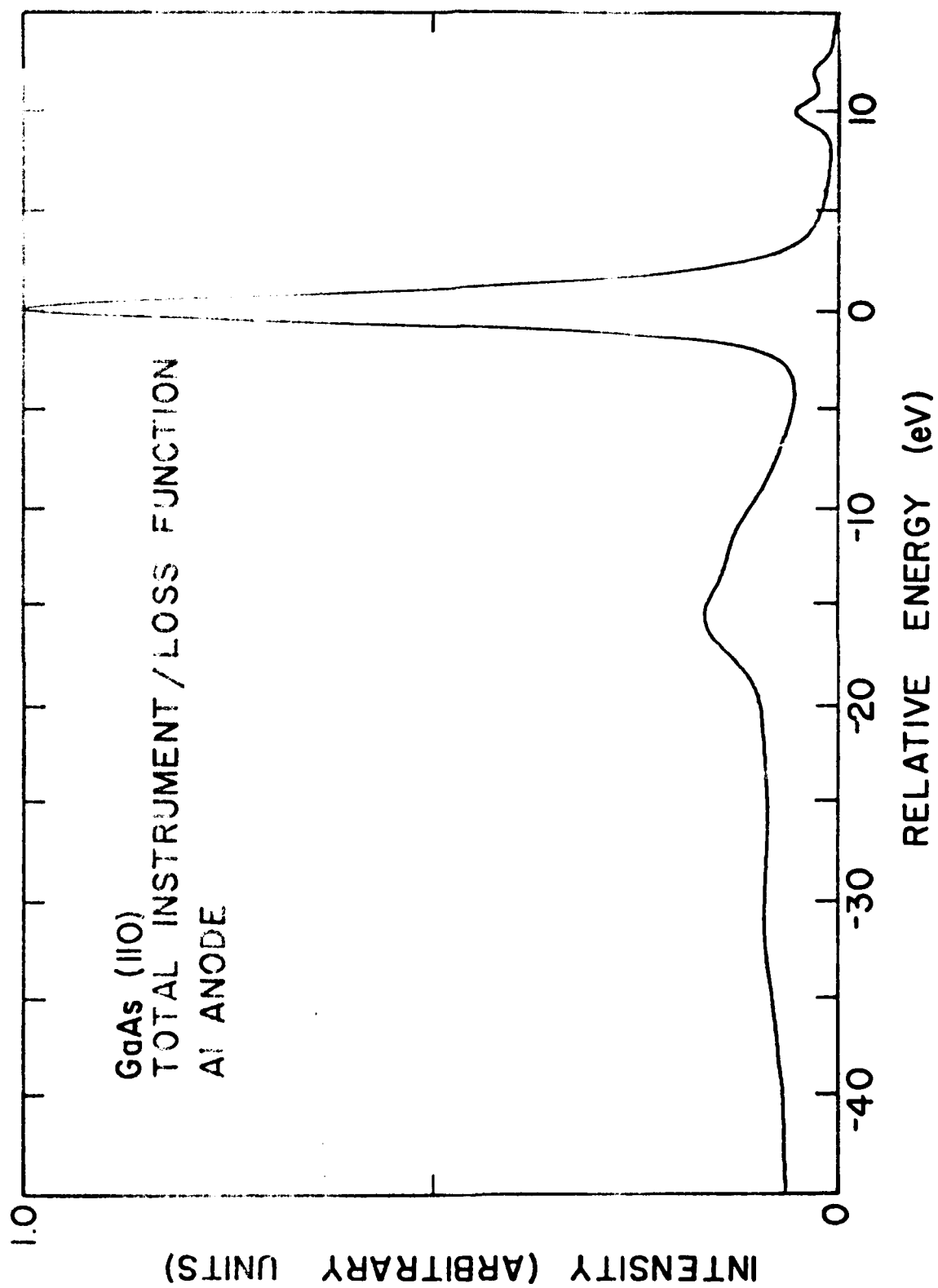


Figure 2.

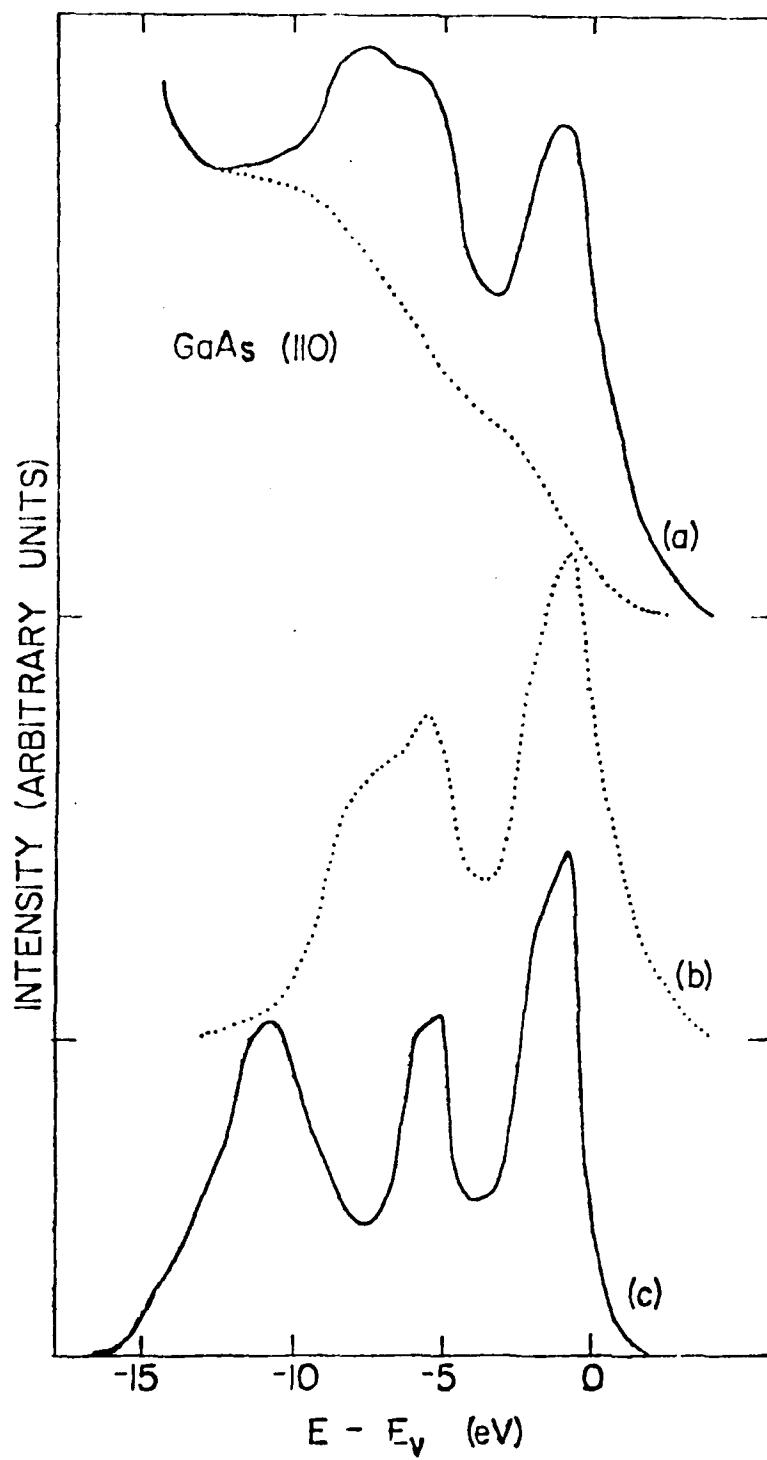


Figure 3.

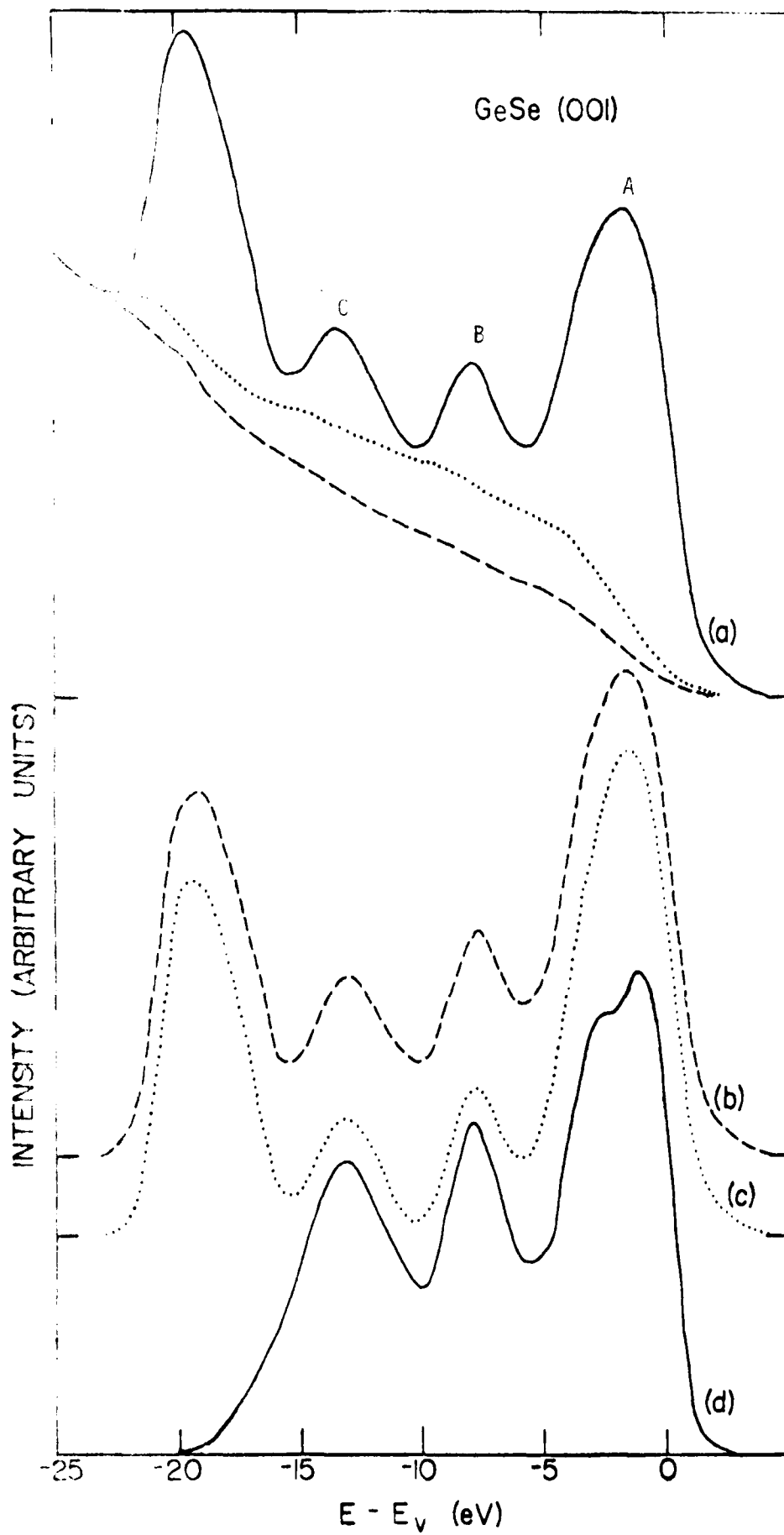


Figure 4.

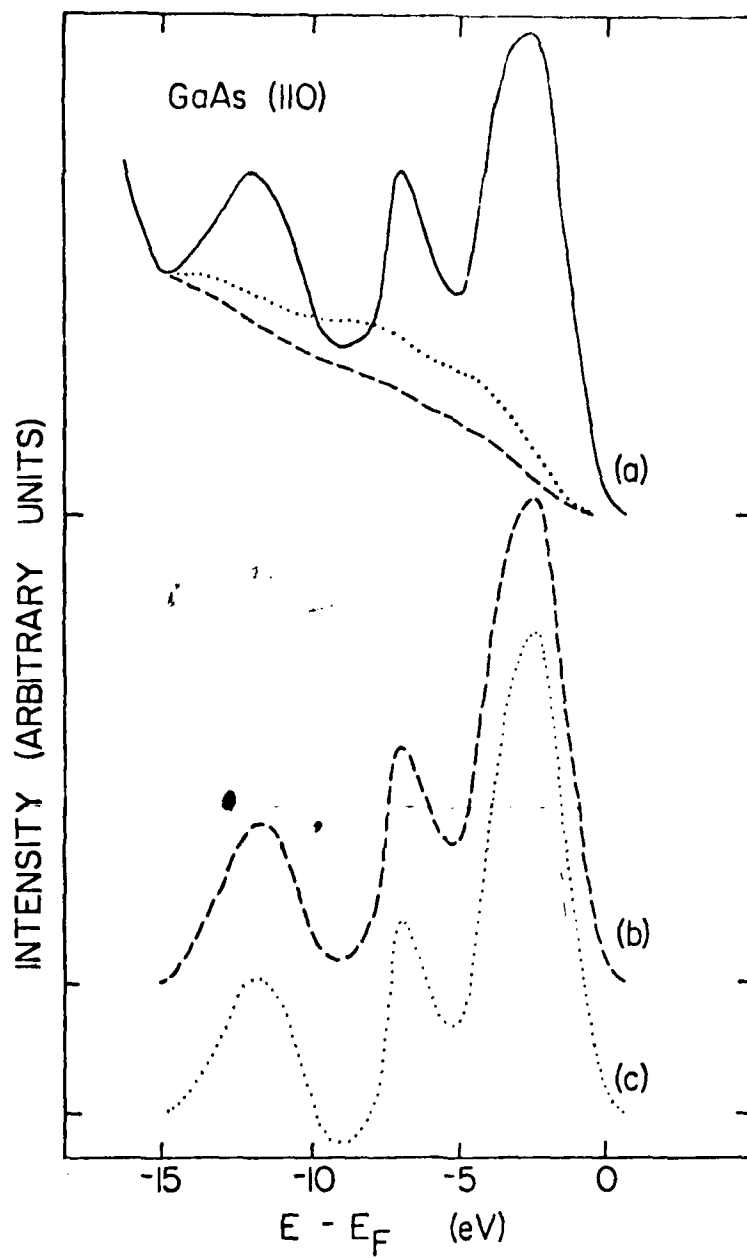


Figure 5.

